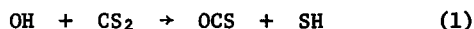


A SIGNIFICANT UPPER LIMIT FOR THE RATE OF FORMATION
OF OCS FROM THE REACTION OF OH WITH CS₂

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Abstract. The rate of reaction of OH with CS₂ to form OCS by reaction (1) has been measured through observation of O¹⁴CS following 254 nm

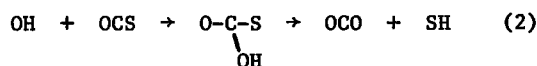
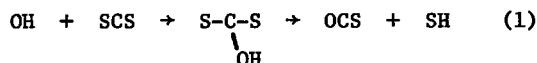


photolysis of mixtures of H₂O₂ with ¹⁴CS₂. The OH concentrations have been monitored through simultaneous measurement in the same cell of either (a) the oxidation of CO to CO₂, or (b) the removal of a hydrocarbon such as C₃H₈ or *iso*-C₄H₁₀. The upper limit for the formation of OCS based on (a) corresponds to a rate constant $k_1 < 0.3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$. Other chemical reactions in the system have led to the formation of both ¹⁴CO and ¹⁴CO₂, indicating the existence of a complex combination of reactions such that the observed O¹⁴CS need not have been formed by (1).

The rate of reaction (1) is sufficiently slow that it is neither an important atmospheric sink for CS₂ nor an important source for atmospheric OCS. The reaction of OH with OCS has not been measured in these experiments, but by analogy with k_1 it is probably not an important atmospheric sink for OCS nor an important source of SO₂.

Introduction

The discovery that both CS₂ (Sandalls and Penkett, 1977) and OCS (Hanst *et al.*, 1975; Maroulis *et al.*, 1977) are present in tropospheric air at the level of $\sim 10^{-10}$ by volume has produced considerable interest in both their sources and sinks (Crutzen, 1976; Sze and Ko, 1979a,b; Logan *et al.*, 1979; Rowland, 1979; Turco *et al.*, 1980). Neither of these compounds undergoes direct solar photodecomposition in the troposphere, although CS₂ does absorb in the near ultraviolet region between 290-380 nm. However, a recent report of rapid, homogeneous gas phase reactions of these molecules with OH radicals (Kurylo, 1978) would represent an important tropospheric sink for each if the report were correct. Kurylo has proposed the reaction mechanisms in (1) and (2) to explain these laboratory observations.



In the absence of any product analysis, the proposed attack of OH on OCS could also be attributed to the simpler, approximately thermoneutral abstraction reaction (3), but the corresponding attack of OH on CS₂ in (4) is endo-

thermic by more than 20 kcal/mole, and cannot be



a fast reaction at the temperature of the measurements (298K). Since the reaction mechanisms for OH reaction are likely to be similar for CS₂ and OCS, the alternate reaction paths of (1) and (2) have been postulated, involving a more complex type of intermediate whose rearrangement ultimately leads to the exothermic formation of SH radicals (Kurylo, 1978; Kurylo and Laufer, 1979; Cox and Sheppard, 1980). If the rate constants measured for OH disappearance in these systems can be correctly assigned to (1) and (2), then the tropospheric attack of OH on CS₂ is both an important sink for CS₂ and an important source of OCS, and the attack of OH on OCS is an important sink for it and an important precursor reaction for the formation of SO₂ in the troposphere (Sze and Ko, 1979a, b; Logan *et al.*, 1979).

The reported values of the rate constant for OH reaction with CS₂ show little agreement with one another, as summarized in Table 1. Comparable disagreement exists for the measurements of the rate constant for OH reaction with OCS (Kurylo, 1978; Atkinson *et al.*, 1978; Wine, Shah and Ravishankara, 1980). In most of these studies, evidence has been sought only for the rate of disappearance of OH, with no observation of removal of its reaction partner (CS₂ or OCS) or of formation of the stable product (OCS or CO₂). No direct evidence exists for rearrangements in the sulfur systems of the kind proposed for (1) and (2) (Kurylo, 1978; Cox and Sheppard, 1980), but a similar rearrangement has been suggested to explain the observed isotopic scrambling of ¹⁸O in the reaction of ¹⁸OH with CO₂ (Kurylo and Laufer, 1979).

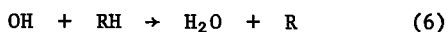
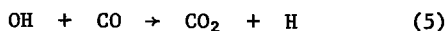
We have sought confirmation of the formation of OCS in the reaction of OH with CS₂, as required by (1), through direct product analysis. Our experiments have been carried out with radioactive ¹⁴CS₂, assaying for O¹⁴CS by radio gas

TABLE 1. Measurements of the Rate Constant for the Reaction of OH with CS₂ to Form O=C=S

Authors	Rate Constant cm ³ molecule ⁻¹ sec ⁻¹
Atkinson <i>et al.</i> , 1978	< 7 x 10 ⁻¹⁴
Kurylo, 1978	18.5±3.4 x 10 ⁻¹⁴
Cox and Sheppard, 1980	43 ±16 x 10 ⁻¹⁴
Wine <i>et al.</i> , 1980	< 0.15 x 10 ⁻¹⁴
This work	< 0.3 x 10 ⁻¹⁴

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chromatography (Wolfgang and Rowland, 1958; Lee *et al.*, 1962). The OH radicals were formed by 254 nm irradiation of H₂O₂ in a system containing about 1-2 torr of H₂O₂; small quantities (1-20 torr) of CO, C₃H₈ or *iso*-C₄H₁₀; and 60-80 torr of ¹⁴CS₂. The overall flux of OH was monitored through the observation of CO₂ formation from the oxidation of CO as in (5), or through diminution in concentration of the hydrocarbon by reaction (6). The rate constants for these reactions are



all convenient for relative measurements of reactions competing with (1) if the latter is proceeding at the rapid rates reported by Kurylo (1978) or by Cox and Sheppard (1980). Our analytical technique is capable of detecting the formation of about 1 part in 10⁵ of O¹⁴CS in ¹⁴CS₂, and of course OCS formed from any other carbon source would not be labeled with ¹⁴C. Earlier laboratory experiments have shown that the molecule OCS can be readily formed under experimental conditions in which both S atoms and CO are present in minuscule concentrations (Lee *et al.*, 1964).

Experimental

Chemicals. Hydrogen peroxide was concentrated to > 95% by room temperature distillation of 90% aqueous H₂O₂ (FMC Corporation), followed by storage at 77K. The radioactive ¹⁴CS₂ was obtained from Amersham with a specific radioactivity of 55 mCi/mmole, and diluted with chromatography CS₂ (Matheson, Coleman and Bell) to a specific activity of 24 μCi/mmole. This mixture contained O¹⁴CS as an impurity (0.07% of total ¹⁴C activity) and was therefore purified by preparative gas chromatography. The CS₂ + ¹⁴CS₂ mixture (designated below as *CS₂) used in photolysis contained < 0.001% each of the total ¹⁴C in the forms of ¹⁴CO, ¹⁴CO₂ and ¹⁴OCS. Carbon monoxide (Matheson Research grade) was purified by passage through a glass bead trap at 77K. The other gases were used as furnished: C₃H₈, Matheson, Instrumental Grade; *iso*-C₄H₁₀, Phillips Research Grade.

Light Sources and Photolysis Cells. Two photolysis arrangements were used. The initial experiments were carried out in a 170 cm³ quartz photolysis cell with suprasil windows, and a 1000-watt Xenon Mercury arc lamp operated through a Bausch & Lomb monochromator for irradiation at 254 nm. All of the experiments listed in Table 2 were performed with a 207 cm³ Vycor 791 cell and an Ultraviolet Products Mineralight R-52 lamp for higher intensity at 254 nm.

Analytical Procedure. After 3-6 hours of photolysis, the samples containing CO, *CS₂ and H₂O₂ were cooled to 77K, and CO (plus O₂ formed during photolysis) were transferred to a silica gel chromatographic loop at 77K. The fraction condensable at 77K was then analyzed by radio gas chromatography (Lee *et al.*, 1962; Iyer, 1973) on a 5-foot Chromosorb-102 column which separated CO₂, OCS and CS₂ in that order. After the elution of the OCS peak, the flow stream was diverted through a glass bead trap at 77K to

prevent proportional counter contamination from the very highly radioactive *CS₂. The ¹⁴CS₂ content was separately assayed with a small aliquot, normally containing only about 1/20 of the sample. The contents of the silica gel loop were analyzed on a 20-foot charcoal column which separates CO from O₂ and N₂.

Similar procedures were used for samples containing *iso*-C₄H₁₀ or C₃H₈ in place of CO. The Chromosorb column was operated at 333K for the separation of OCS from C₃H₈, and at 358K for the separation of *iso*-C₄H₁₀ and OCS.

A typical filling of the cell to 50 torr pressure of *CS₂ corresponded to approximately 4 × 10⁶ counts min⁻¹ measured at a flow rate of 30 ml per minute through the counter.

Results

For each experiment, a percentage conversion of ¹⁴CS₂ to O¹⁴CS can be measured and compared with the percentage change of CO to CO₂ or percentage removal of RH. Typical data for all three of these types of experiments are summarized in Table 2. In each case, the presence of other oxidized forms of ¹⁴C (¹⁴CO and ¹⁴CO₂) demonstrates that a variety of chemical reactions are occurring in these photolysis systems, and the observation of O¹⁴CS therefore does not demonstrate that reaction (1) must be occurring, since other reaction routes could be forming O¹⁴CS as well as ¹⁴CO and ¹⁴CO₂. Macroscopic amounts of CO₂ and OCS were always observed as well. The experimental observations of yields of O¹⁴CS are converted into upper limits for the absolute rate constant for k₁ through the known reaction rate constants for k₅ (NASA, 1979) and k₆ (Gorse and Volman, 1974; Butler *et al.*, 1978).

Discussion

Our experiments have consistently shown that O¹⁴CS is not formed by the reaction of OH with ¹⁴CS₂ at any rate comparable to the rates reported by Kurylo (1978) and by Cox and Sheppard (1980). A conservative upper limit from six separate experiments with CO as the monitor at 298K is k₁ < 0.3 × 10⁻¹⁴ cm³ molecule⁻¹ sec⁻¹, with one experiment at 313K putting the limit at 0.1 × 10⁻¹⁴ cm³ molecule⁻¹ sec⁻¹. Equivalent results were obtained with both light sources. The experiments with C₃H₈ and *iso*-C₄H₁₀ as monitors also show k₁ to be much less than measured by Kurylo (1978) and by Cox and Sheppard (1980). In all cases, other chemical processes than (1) are possible leading to the formation of O¹⁴CS, so that there is no requirement that k₁ be other than zero. Since reaction (4) is endothermic, our upper limit on k₁ is also an upper limit for the overall reaction rate of OH with CS₂. The insertion of this upper limit into various atmospheric models leads to the conclusions that: (a) CS₂ is not an important precursor for OCS in the atmosphere; and (b) reaction with OH is not an important route for the removal of CS₂ from the earth's atmosphere.

Several of the experimental measurements summarized in Table 1 are based upon comparative OH removal rates in the absence and presence of added CS₂ during the flash photolysis of H₂O, without measurement of concentration changes for

TABLE 2. Typical Experimental Results in the 254 nm Photolysis of H₂O₂-CS₂ Mixtures

Pressure, torr					
H ₂ O ₂	0	0.9 ^(a)	1.4	1.8	1.8
*CS ₂	53.4	50.2	53.6	70.1	66.1
CO	20.1	18.6	20.0	0	0
C ₃ H ₈	0	0	0	2.0	0
iso-C ₄ H ₁₀	0	0	0	0	1.7
Observed Radioactivity in Product, % of Total ¹⁴ C					
¹⁴ CO	0.084	0.936	2.09	(n.m.)	0.589
¹⁴ CO ₂	0.006	0.069	0.63	0.118	0.053
O ¹⁴ CS	0.009	0.021	0.15	0.106	0.066
%CO + CO ₂	1.2	3.1	7.9	-	-
%RH removed	-	-	-	18.3	17.4
Δ(Monitor)/Δ(OCS)					
k ₅ /k ₁	-	150	50	-	-
k ₆ /k ₁	-	-	-	170	260
k ₁ , 10 ⁻¹⁴					
cm ³ molecule ⁻¹ sec ⁻¹		≤ 0.1	≤ 0.3	≤ 0.9	≤ 0.8

(a) Temperature 313K for this experiment; others at 298K.

k₅ = 1.5 × 10⁻¹³ cm³ molecule⁻¹ sec⁻¹ (NASA, 1979) at 0.1 atmosphere.

k₆ = 1.6 × 10⁻¹² cm³ molecule⁻¹ sec⁻¹ (Butler *et al.*, 1978) for i-C₄H₁₀.

k₆ = 2.2 × 10⁻¹² cm³ molecule⁻¹ sec⁻¹ (Gorse and Volman, 1974) for C₃H₈.

n.m. = not measured

CS₂, OCS or SH. These photolytic systems also involve the photodecomposition of CS₂ when it is present, with the release of S atoms. The relative extent of photolysis of CS₂ versus the OH source was lowest in the experiments of Wine *et al.*, (1980), who observed essentially no increase in OH removal rate with added CS₂.

We believe that plausible alternate mechanisms exist for the increased disappearance rate for OH found by Kurylo (1978) and for CS₂ by Cox and Sheppard (1980), including the possibility of OH reaction with fragments from CS₂ photolysis, i.e., OH + S and OH + CS. The latter combination may be the pathway by which O¹⁴CS is formed in our experiments, and for the OCS found by Cox and Sheppard.

The use of a very different kinetic measurement technique in our experiments has the advantage that our sensitivities to impurities are unlike those encountered in flash-photolysis OH-disappearance measurements. In particular, the reaction of OH with trace levels of H₂S has no important consequence in our system, except a lowering of the concentration of OH radicals available for reactions (1), (5) and (6). Since no ¹⁴C is involved in that reaction, no O¹⁴CS can be formed. On the other hand, the reaction of OH with H₂S with a rate constant of 3 × 10⁻¹² cm³ molecule⁻¹ sec⁻¹ (NBS, 1977) is sufficiently rapid that an H₂S/CS₂ ratio of 10⁻³ in a flashed CS₂/H₂O mixture can explain an apparent rate constant of 3 × 10⁻¹⁵ cm³ molecule⁻¹ sec⁻¹ for the disappearance of OH in a CS₂ system.

While we have not performed any experiments

here which relate to the reaction of OH with OCS, the positive evidence for reaction (2) and/or (3) with OCS has been obtained by Kurylo (1978) by the same technique used for gathering the CS₂ data of Table 1. With OCS as the reactant for OH, Cox and Sheppard have reported that essentially no reaction is observed, in marked contrast to their results with CS₂. Wine *et al.*, (1980) have also reported that no rapid reaction is observed. We conclude that the reaction of OH with OCS in all probability does not proceed at a rapid rate, and therefore that: (a) reaction with OH is not an important tropospheric sink for OCS; and (b) OCS is not an important tropospheric precursor of SO₂. The ultraviolet photolysis of OCS in the stratosphere can be a source of SO₂ through the subsequent reactions of the atomic S released during photodecomposition (Crutzen, 1976).

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